Electronic supplementary information

2,2'-Biphen[*n*]arenes (*n* = 4–8): one-step, high-yield synthesis and host–guest properties

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Experimental

Materials and methods

Organic cationic guests $\mathbf{1}^{+}$–$\mathbf{4}^{2+}$ with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate counter anions were prepared from their chloride or bromide salts using our previously reported methods.[S1] ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV500 instrument. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Melting points were obtained on an X-4 digital melting point apparatus without correction.

Synthesis of 2,2'-EtBP*n*s

To the solution of 2,2'-diethoxybiphenyl (4.8 g, 20 mmol) in CH_2ClCH_2Cl (200 mL) was added paraformaldehyde (0.90 g, 30 mmol). Boron trifluoride diethyl etherate (5.0 ml, 40 mmol) was then added to the reaction mixture. The mixture was stirred at 25 °C for 30 minutes. Then the reaction was quenched by addition of 100 mL water. The organic phase was separated and washed with saturated aqueous $NaHCO_3$, and water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (eluent: 10/1, v/v, Petroleum ether:ethyl acetate gradually changing to 2/1) to afford **2,2'-EtBP4** (0.80 g, 16%), **2,2'-EtBP5** (0.72 g, 14%), **2,2'-EtBP6** (0.42 g, 8.4%), **2,2'-EtBP7** (0.32 g, 6.4%), and **2,2'-EtBP8** (0.30 g, 5.9%) as white solids.

2,2'-EtBP4. m.p.108–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.14–6.98 (m, 16H), 6.80 (d, *J* = 8.3 Hz, 8H), 3.91 (q, *J* = 7.0 Hz, 16H), 3.85 (s, 8H), 1.18 (t, *J* = 7.0 Hz, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 154.8, 133.2, 132.3, 128.5, 128.3, 112.3 (C of biphenyl), 64.1 (C of methylene in ethoxy group), 40.4 (C of methylene bridge) 14.9 (C of methyl in ethoxy group). HRMS (ESI): $C_{68}H_{72}O_8Na^{+}$, calcd m/z 1039.5104; found m/z 1039.5117.

2,2'-EtBP5. m.p.86–88 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.10–6.98 (m, 20H), 6.78 (d, *J* = 8.3 Hz, 10H), 3.86 (dd, *J* = 13.9, 6.9 Hz, 30H), 1.13 (t, *J* = 7.0 Hz,30H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 154.7, 133.1, 132.3, 128.4, 128.0, 112.4 (C of biphenyl), 64.0 (C of methylene in ethoxy group), 40.5 (C of methylene

bridge), 14.8 (C of methyl in ethoxy group). HRMS (ESI): $C_{85}H_{90}O_{10}Na^+$, calcd m/z 1293.6405; found m/z 1293.6234.

2,2'-EtBP6. m.p. 90–92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.08 (d, *J* = 2.2 Hz, 12H), 7.03 (dd, *J* = 8.3, 2.2 Hz, 12H), 6.78 (d, *J* = 8.4 Hz, 12H), 3.85 (dd, *J* = 13.6, 6.6 Hz, 36H), 1.12 (t, *J* = 7.0 Hz, 36H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 154.6, 133.1, 132.4, 128.4, 128.0, 112.4 (C of biphenyl), 64.0 (C of methylene in ethoxy group), 40.4 (C of methylene bridge), 14.8 (C of methyl in ethoxy group). HRMS (ESI): $C_{102}H_{108}O_{12}Na^+$, calcd m/z 1547.7706; found m/z 1547.7764.

2,2'-EtBP7. m.p.97–100 °C**.** ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.09 (d, *J* = 2.2 Hz, 14H), 7.03 (dd, *J* = 8.3, 2.2 Hz, 14H), 6.78 (d, *J* = 8.4 Hz, 14H), 3.85 (dd, *J* = 13.8, 6.8 Hz, 42H), 1.12 (t, *J* = 7.0 Hz, 42H).^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 154.6, 133.1, 132.3, 128.4, 127.9, 112.4 (C of biphenyl), 63.98 (C of methylene in ethoxy group), 40.4 (C of methylene bridge), 14.8 (C of methyl in ethoxy group). HRMS (ESI): $C_{119}H_{126}O_{14}Na^+$, calcd m/z 1802.9079; found m/z 1802.9056.

2,2'-EtBP8. m.p. 92–95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.10 (d, *J* = 2.2 Hz, 16H), 7.03 (dd, *J* = 8.4, 2.2 Hz, 16H), 6.78 (d, *J* = 8.4 Hz, 16H), 3.86 (dd, *J* = 13.9, 6.9 Hz, 48H), 1.12 (t, *J* = 7.0 Hz, 48H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 154.6, 133.1, 132.4, 128.4, 128.0, 112.4 (C of biphenyl), 64.0 (C of methylene in ethoxy group), 40.4 (C of methylene bridge), 14.8 (C of methyl in ethoxy group). HRMS (ESI): $C_{136}H_{144}O_{16}NH_4^+$, calcd m/z 2052.0832; found m/z 2052.0833.

Copies of ^{1}H NMR and ^{13}C NMR spectra of the new macrocycles.

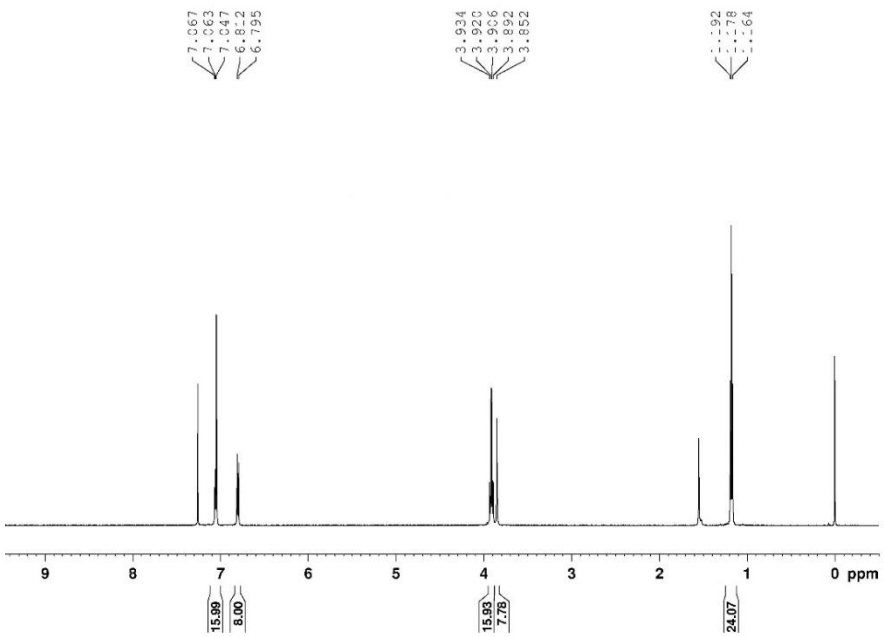

Figure S1. ^{1}H NMR spectrum (500 MHz) of **2,2'-EtBP4** in $CDCl_3$

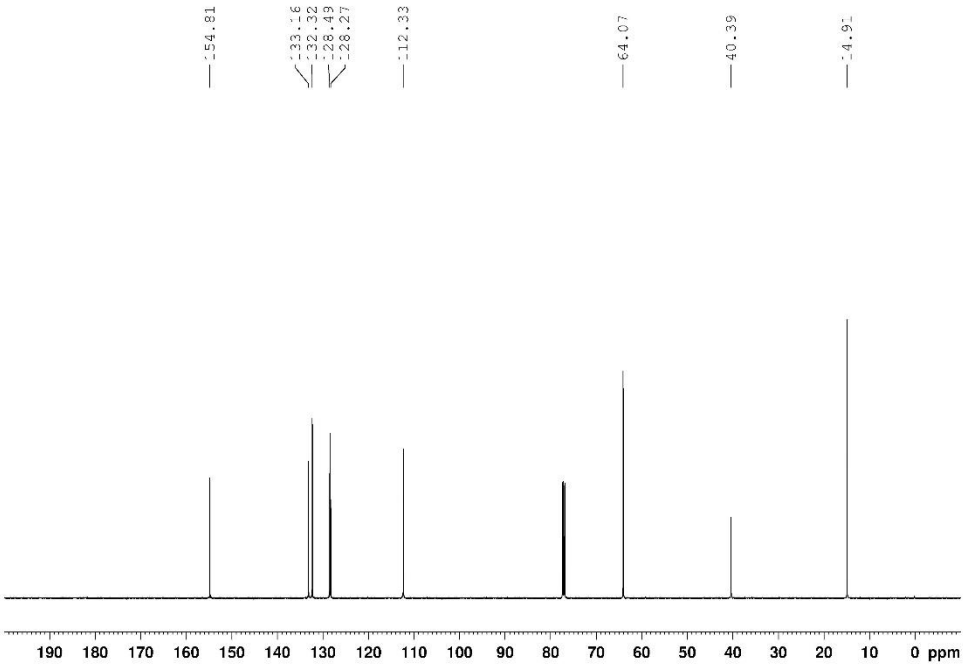

Figure S2. ^{13}C NMR spectrum (125 MHz) of **2,2'-EtBP4** in $CDCl_3$

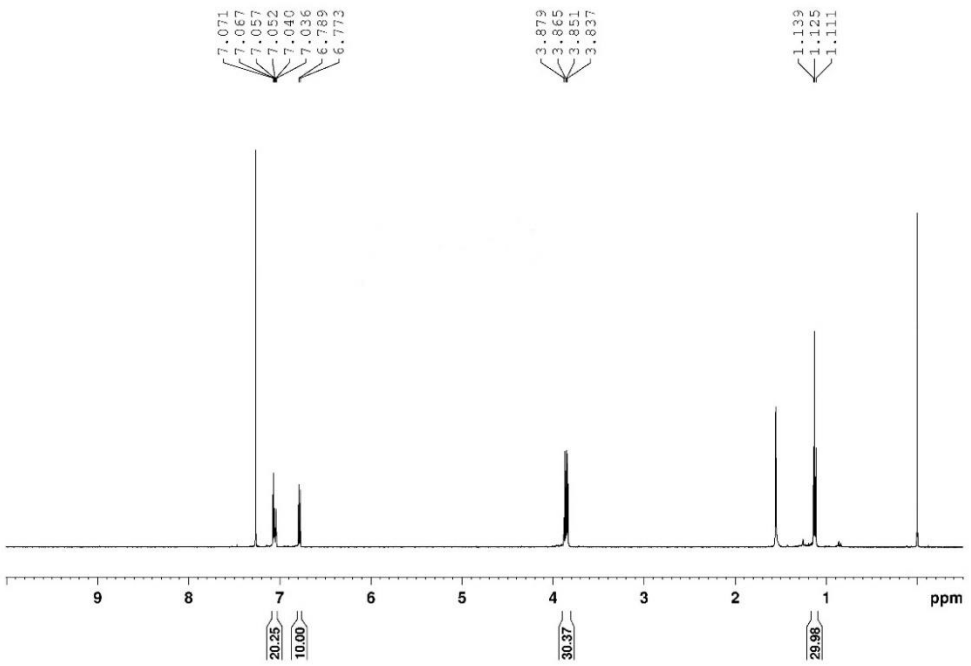

Figure S3. ^{1}H NMR spectrum (500 MHz) of **2,2'-EtBP5** in $CDCl_3$

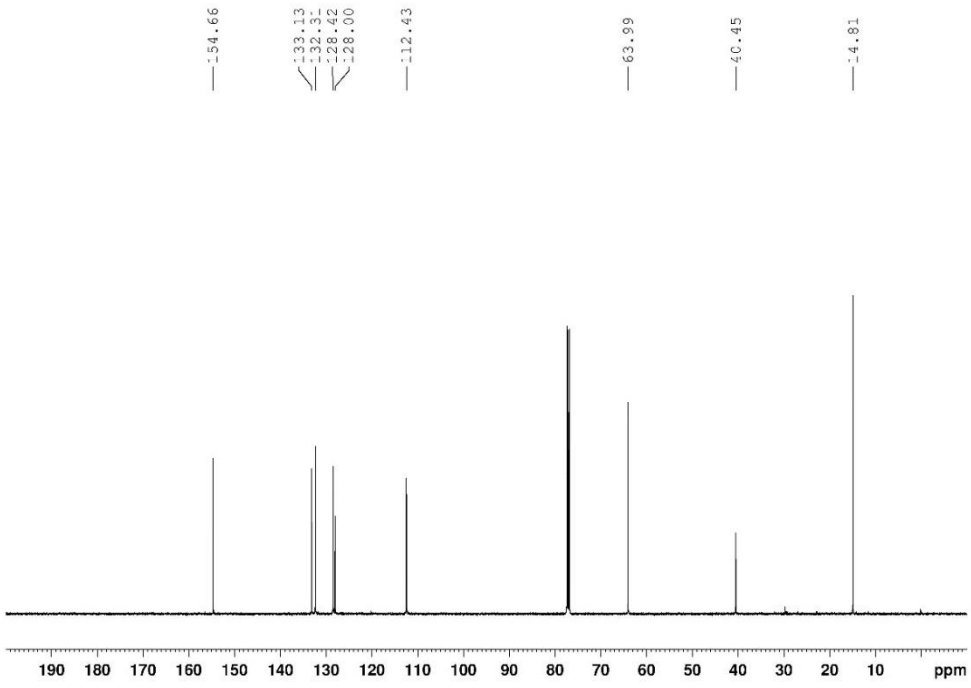

Figure S4. ^{13}C NMR spectrum (125 MHz) of **2,2'-EtBP5** in $CDCl_3$

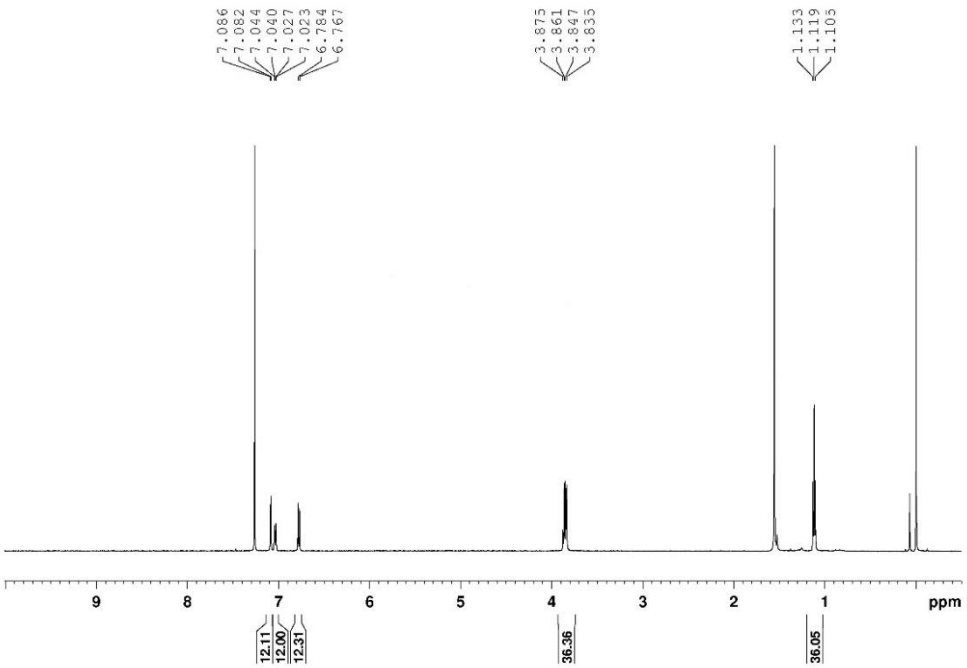

Figure S5. ^{1}H NMR spectrum (500 MHz) of **2,2'-EtBP6** in $CDCl_3$

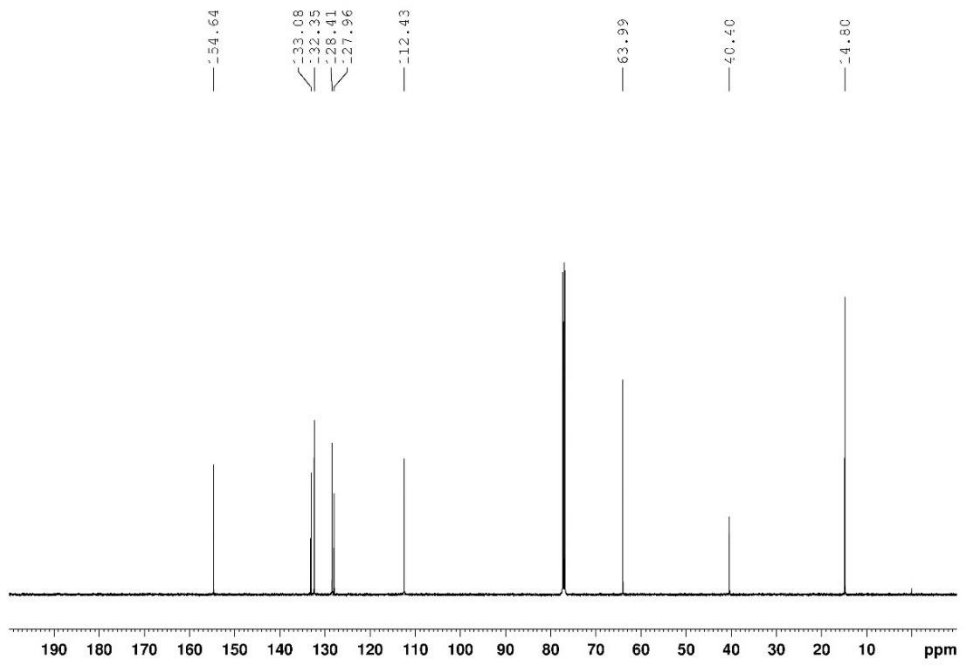

Figure S6. ^{13}C NMR spectrum (125 MHz) of **2,2'-EtBP6** in $CDCl_3$.

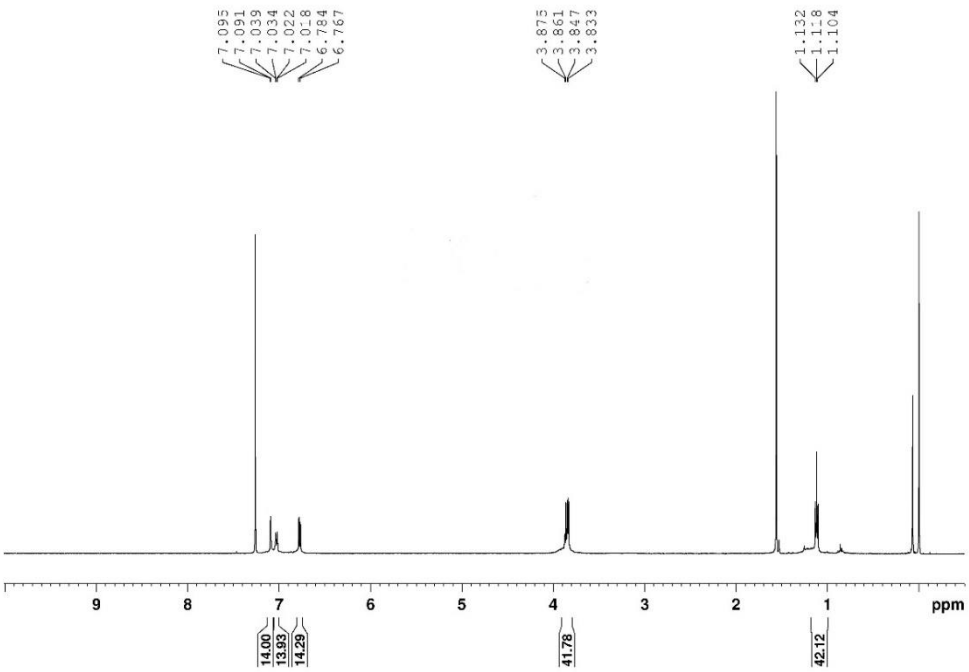

Figure S7. ^{1}H NMR spectrum (500 MHz) of **2,2'-EtBP7** in $CDCl_3$.

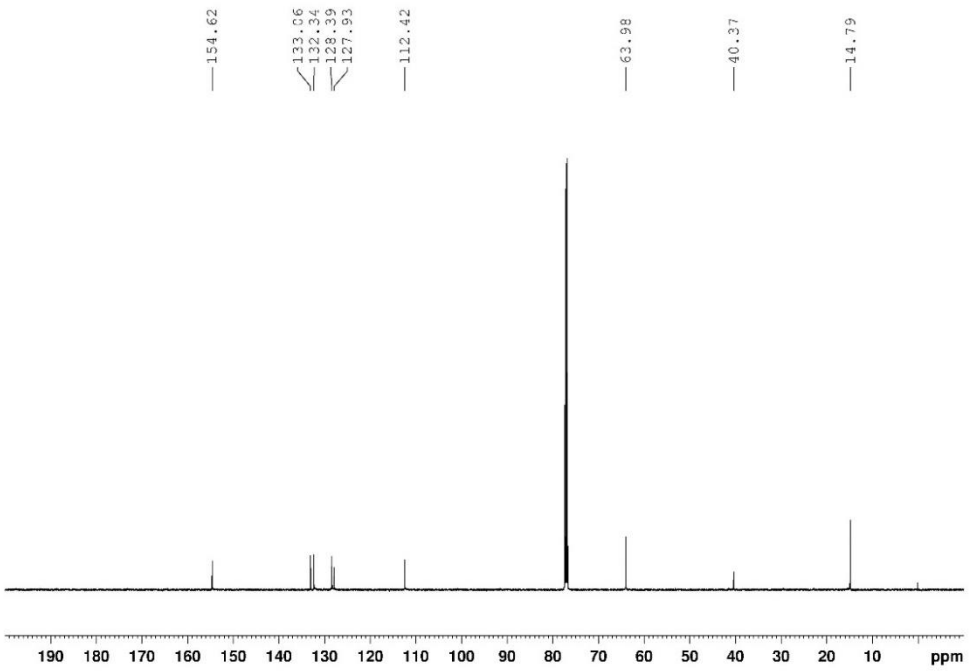

Figure S8. ^{13}C NMR spectrum (125 MHz) of **2,2'-EtBP7** in $CDCl_3$.

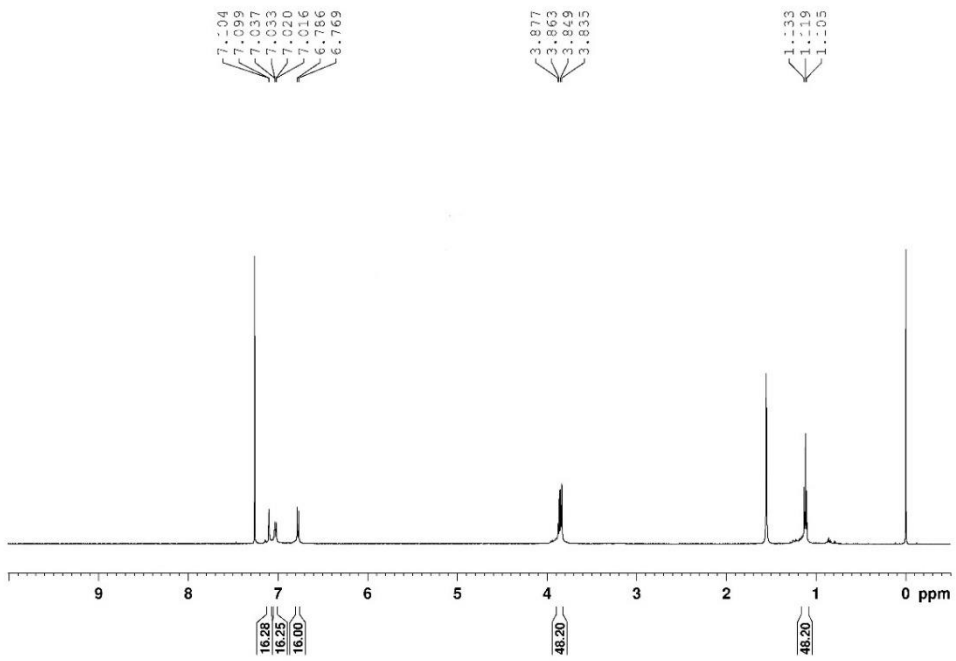

Figure S9. ^{1}H NMR spectrum (500 MHz) of **2,2'-EtBP8** in $CDCl_3$.

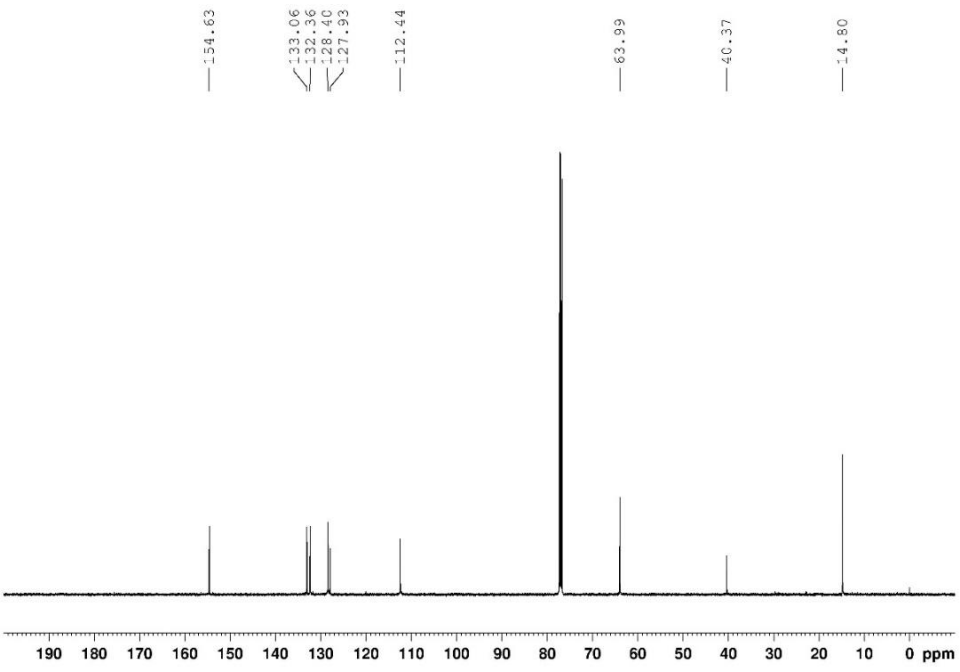

Figure S10. ^{13}C NMR spectrum (125 MHz) of **2,2'-EtBP8** in $CDCl_3$.

VT ^{1}H NMR spectra of 2,2'-EtBP4 and 2,2'-EtBP8.

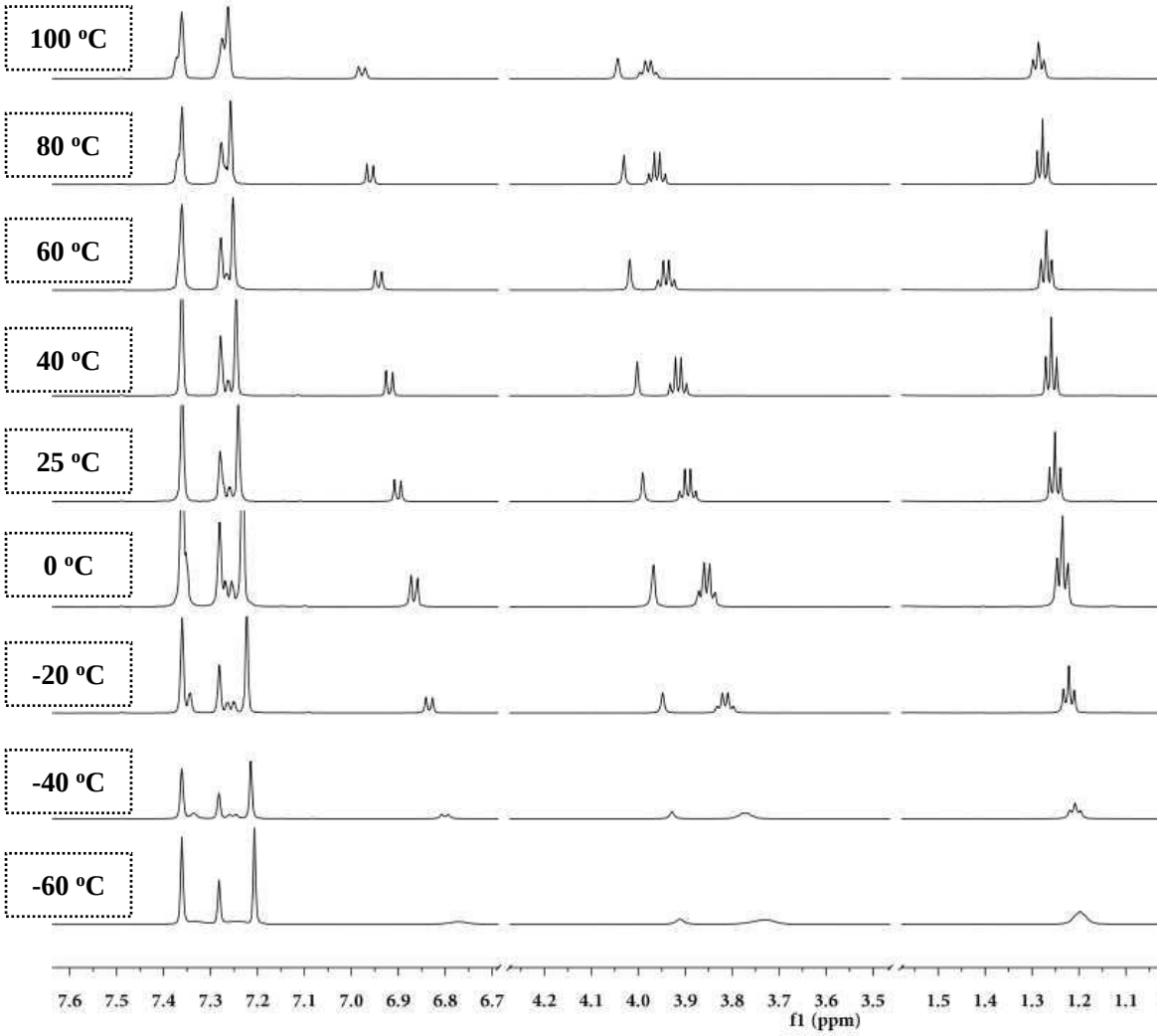

Figure S11. VT ^{1}H NMR spectra of **2,2'-EtBP4** in toluene-d_8 in the temperature range from –60 ºC to 100 ºC.

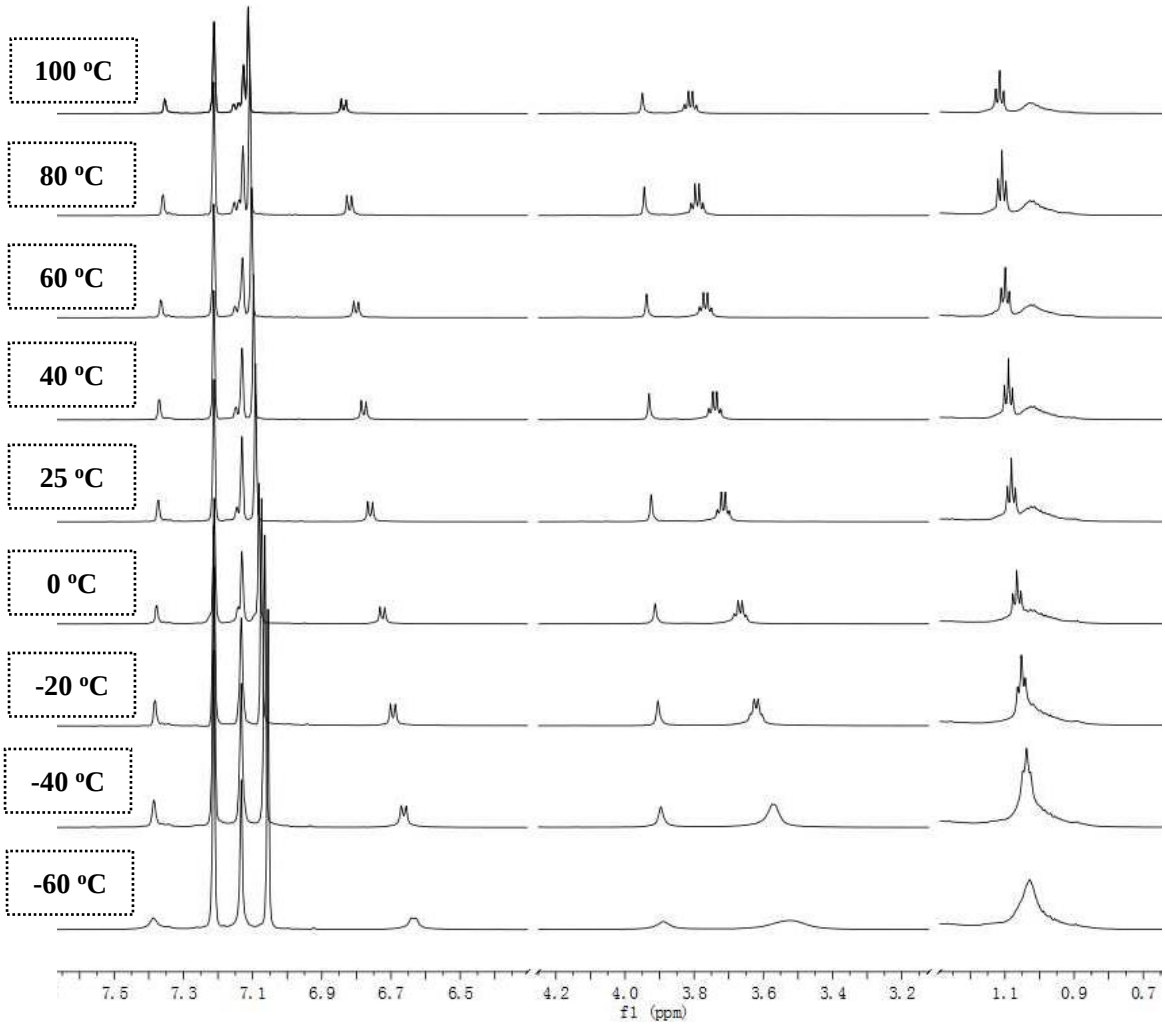

Figure S12. VT ^{1}H NMR spectra of **2,2'-EtBP8** in toluene-d_8 in the temperature range from –60 ºC to 100 ºC.

Additional ^{1}H NMR spectra of host-guest mixture.

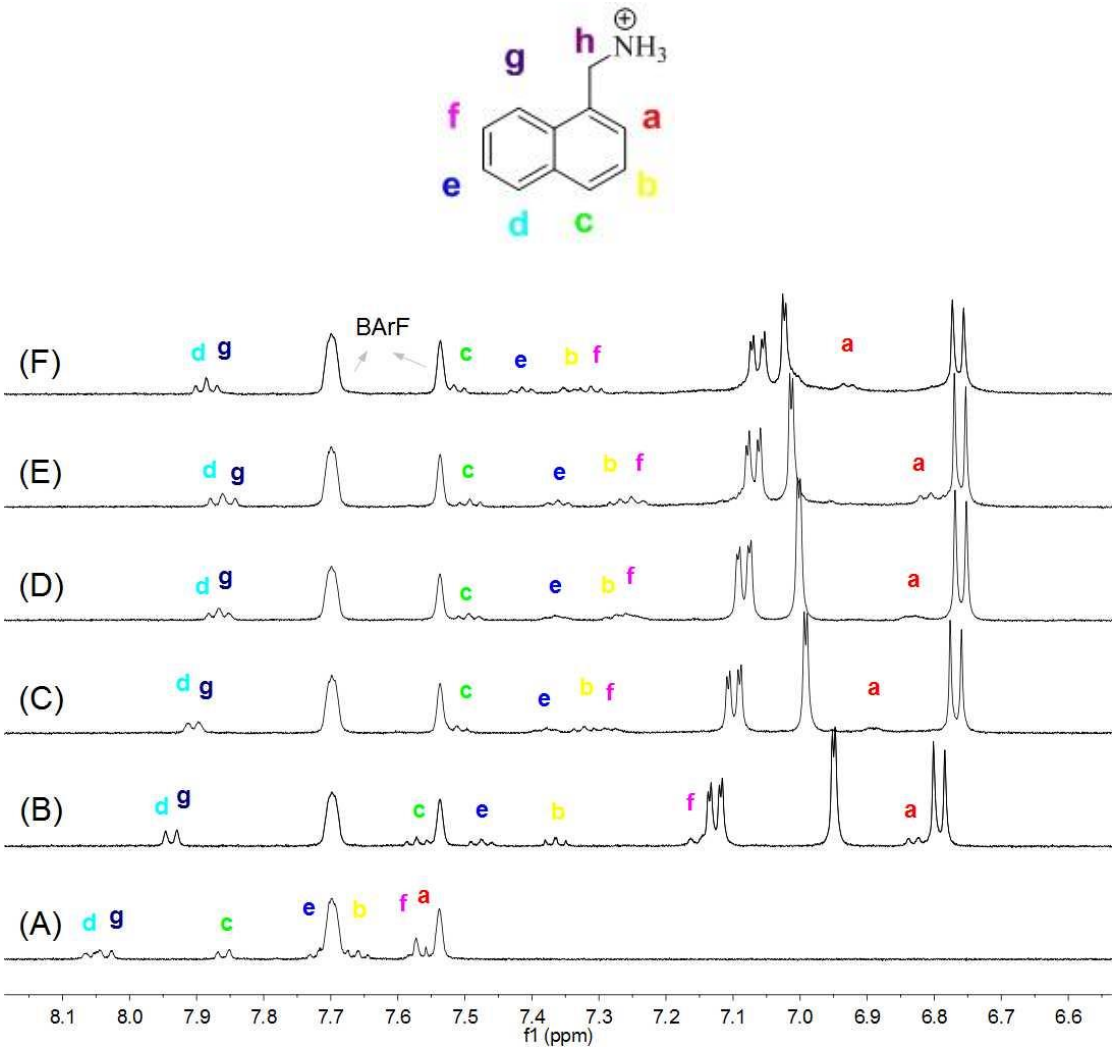

Figure S13. ^{1}H NMR spectra (500 MHz, 298 K) of $\mathbf{2}^{+}$ (2.0 mM) in CD_2Cl_2 in the absence (A) and presence of ~1.0 equiv. of **2,2'-EtBP4** (B), **2,2'-EtBP5** (C), **2,2'-EtBP6** (D), **2,2'-EtBP7** (E), and **2,2'-EtBP8** (F).

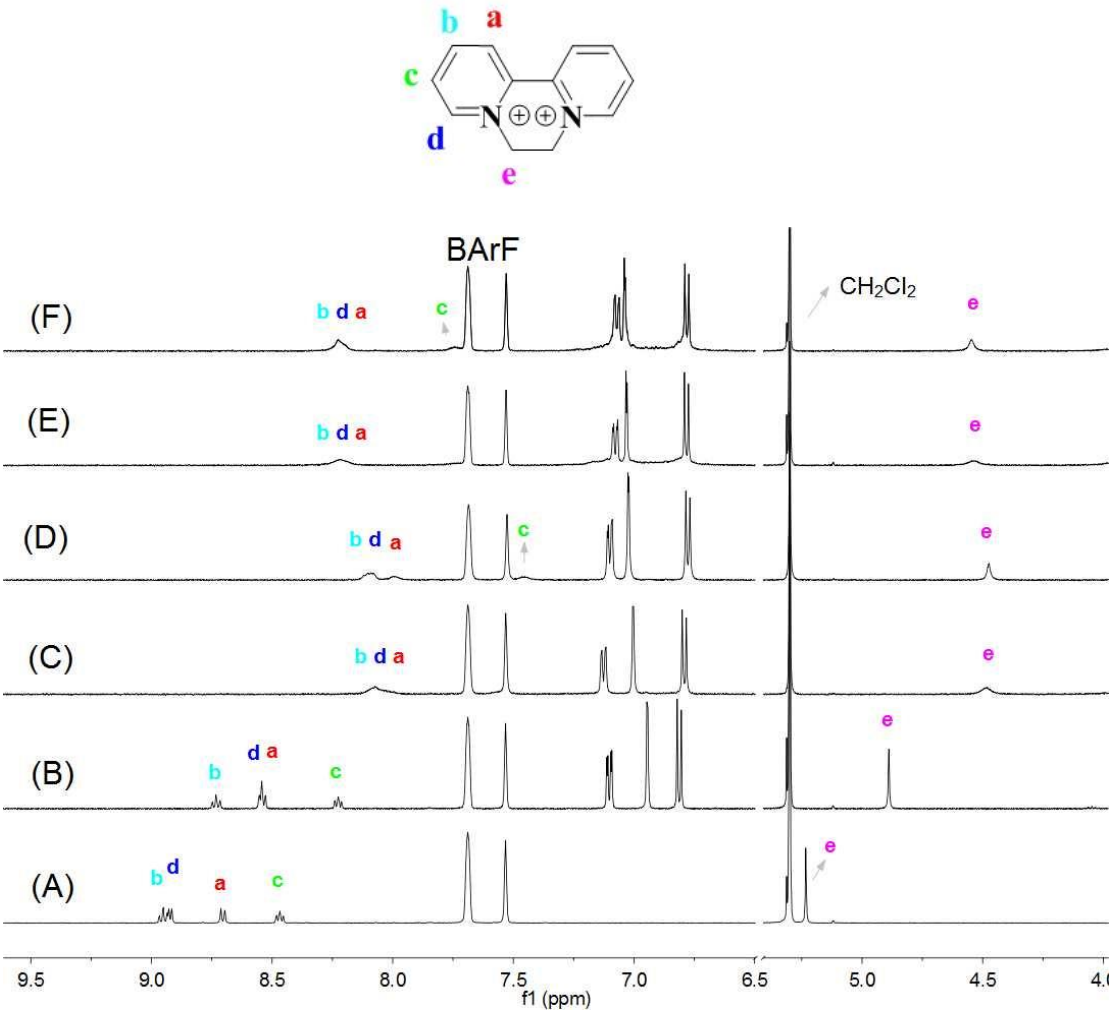

Figure S14. ^{1}H NMR spectra (500 MHz, 298 K) of $\mathbf{3}^{2+}$ (2.0 mM) in CD_2Cl_2 in the absence (A) and presence of ~1.0 equiv. of **2,2'-EtBP4** (B), **2,2'-EtBP5** (C), **2,2'-EtBP6** (D), **2,2'-EtBP7** (E), and **2,2'-EtBP8** (F).

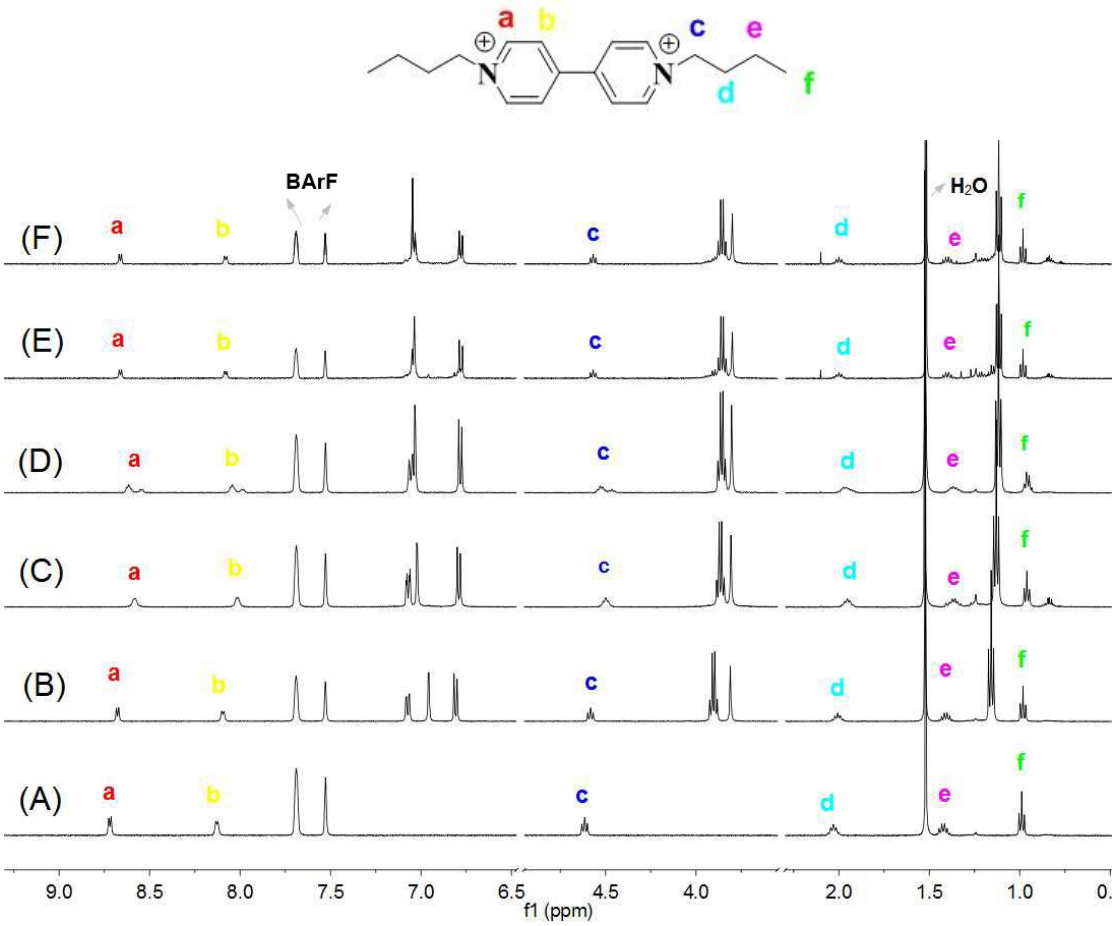

Figure S15. ^{1}H NMR spectra (500 MHz, 298 K) of $\mathbf{4}^{2+}$ (2.0 mM) in CD_2Cl_2 in the absence (A) and presence of ~1.0 equiv. of **2,2'-EtBP4** (B), **2,2'-EtBP5** (C), **2,2'-EtBP6** (D), **2,2'-EtBP7** (E), and **2,2'-EtBP8** (F).

Molar ratio plots and determination of K_a.

In the present host-guest systems, chemical exchange is fast on the NMR time scale. To determine the association constants (K_a), ^{1}H NMR titrations were performed in CD_2Cl_2 with solutions which had a constant concentration of 2,2'-EtBP*n* host and varying concentrations of guest. Assuming 1 : 1 binding stoichiometry between 2,2'-EtBP*n*s and these guests, the K_a values could be calculated by analyzing the sequential changes in chemical shift changes of 2,2'-EtBP*n* host that occurred with changes in guest concentration by using the nonlinear curve-fitting method from the following equation[S2]:

$$A = (A_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0+1/K_a) - (0.5\ ([G]_0^2 + (2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5}))$$

Where A is the chemical shift change of aromatic protons on 2,2'-EtBP*n* host at $[G]_0$, A_∞ is the chemical shift change when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the 2,2'-EtBP*n* host, and $[G]_0$ is the initial concentration of guest.

For each host−guest pair examined, the plot of Δδ as a function of $[G]_0$ gave an excellent fit (Figure S16~S20), verifying the validity of the 1:1 binding stoichiometry assumed. Additionally, mole ratio plots were also made (Figure S21~25); they proved consistent with the proposed 1 : 1 host–guest binding stoichiometry.

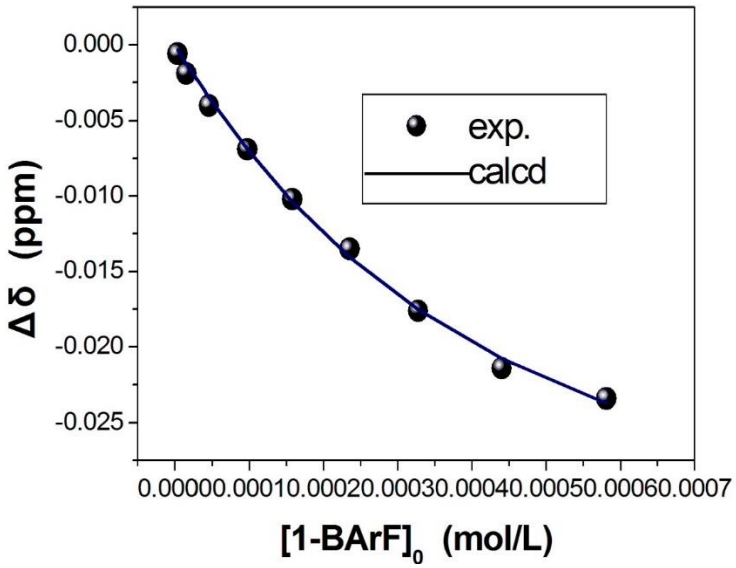

Figure S16. The non-linear curve-fitting (NMR titrations) for the complexation of **2,2'-EtBP4** (2.0×10^{-4} mol/L) with and guest $\mathbf{1}^+$ in CD_2Cl_2 at 298 K.

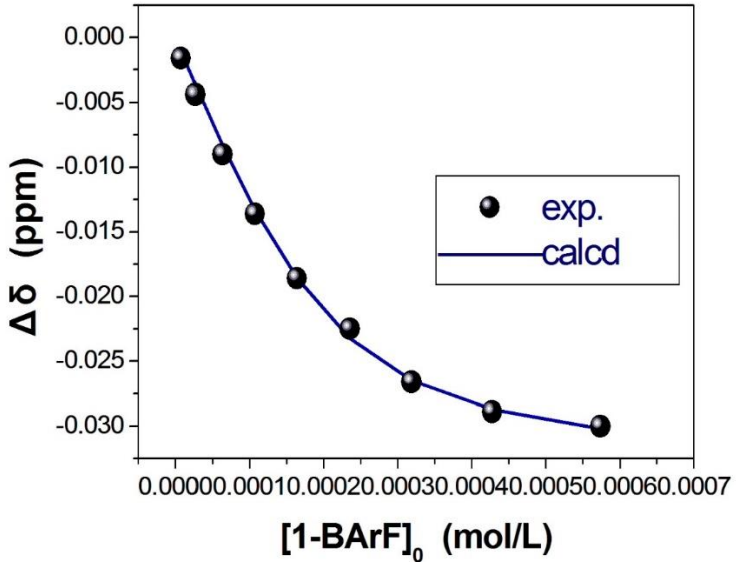

Figure S17. The non-linear curve-fitting (NMR titrations) for the complexation of **2,2'-EtBP5** (2.0×10^{-4} mol/L) with and guest $\mathbf{1}^+$ in CD_2Cl_2 at 298 K.

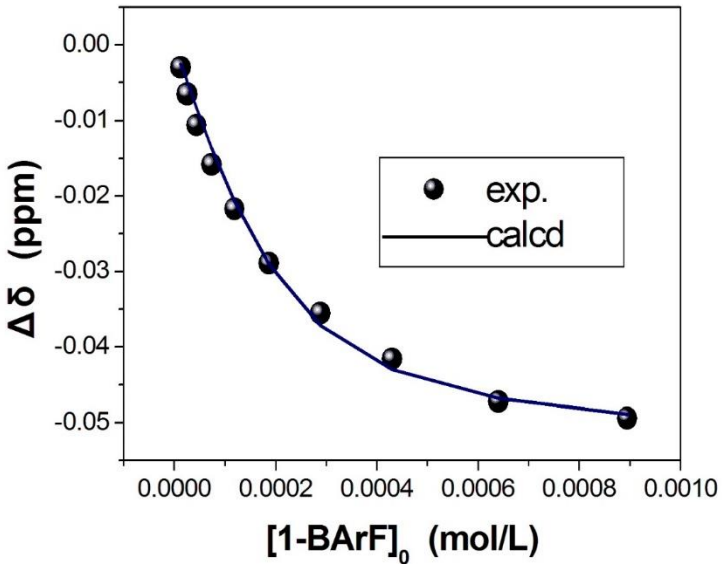

Figure S18. The non-linear curve-fitting (NMR titrations) for the complexation of **2,2'-EtBP6** (2.0×10^{-4} mol/L) with and guest $\mathbf{1}^+$ in CD_2Cl_2 at 298 K.

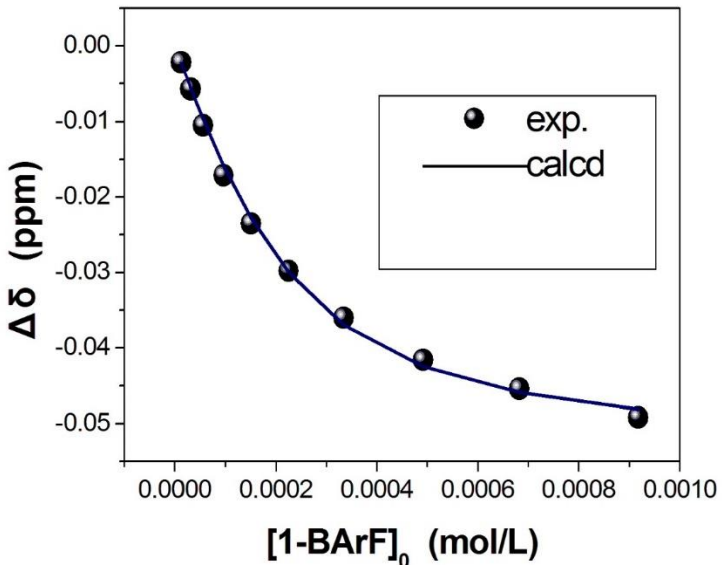

Figure S19. The non-linear curve-fitting (NMR titrations) for the complexation of **2,2'-EtBP7** (2.0×10^{-4} mol/L) with and guest $\mathbf{1}^+$ in CD_2Cl_2 at 298 K.

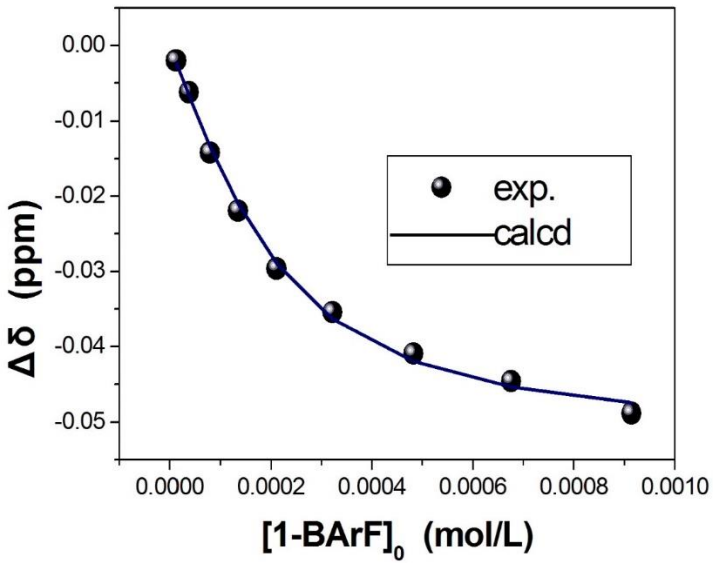

Figure S20. The non-linear curve-fitting (NMR titrations) for the complexation of **2,2'-EtBP8** (2.0×10^{-4} mol/L) with and guest $\mathbf{1}^+$ in CD_2Cl_2 at 298 K.

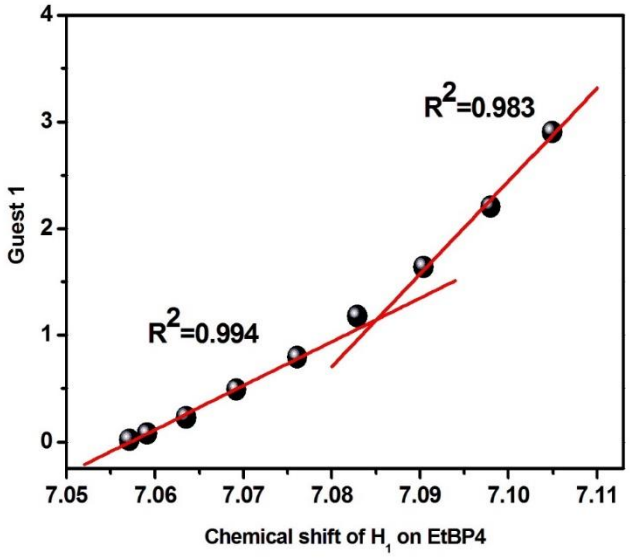

Figure S21. Mole ratio plot for **2,2'-EtBP4** and $\mathbf{1}^+$ from ^{1}H NMR (500 MHz, 298 K) experiments, wherein **2,2'-EtBP4** (at a fixed concentration) in CD_2Cl_2 was treated different molar equivalents of $\mathbf{1}^+$. The results are consistent with a 1 : 1 binding stoichiometry.

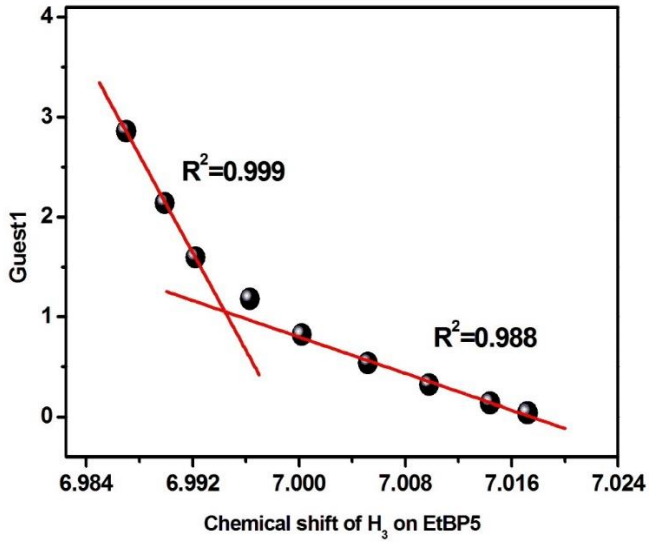

Figure S22. Mole ratio plot for **2,2'-EtBP5** and $\mathbf{1}^+$ from ^{1}H NMR (500 MHz, 298 K) experiments, wherein **2,2'-EtBP5** (at a fixed concentration) in CD_2Cl_2 was treated different molar equivalents of $\mathbf{1}^+$. The results are consistent with a 1 : 1 binding stoichiometry.

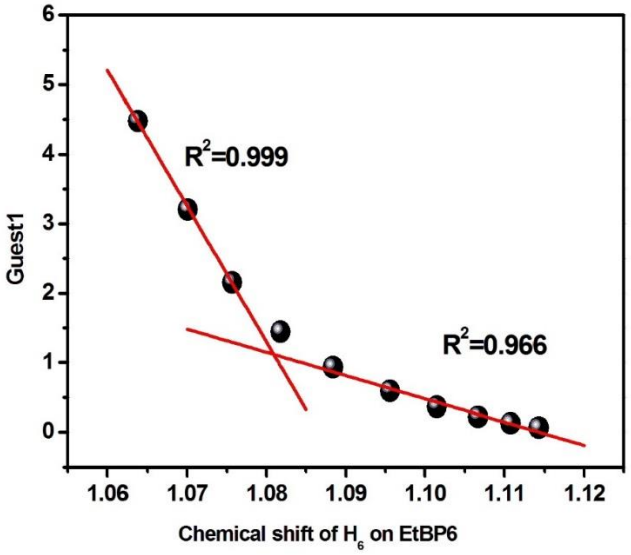

Figure S23. Mole ratio plot for **2,2'-EtBP6** and $\mathbf{1}^+$ from ^{1}H NMR (500 MHz, 298 K) experiments, wherein **2,2'-EtBP6** (at a fixed concentration) in CD_2Cl_2 was treated different molar equivalents of $\mathbf{1}^+$. The results are consistent with a 1 : 1 binding stoichiometry.

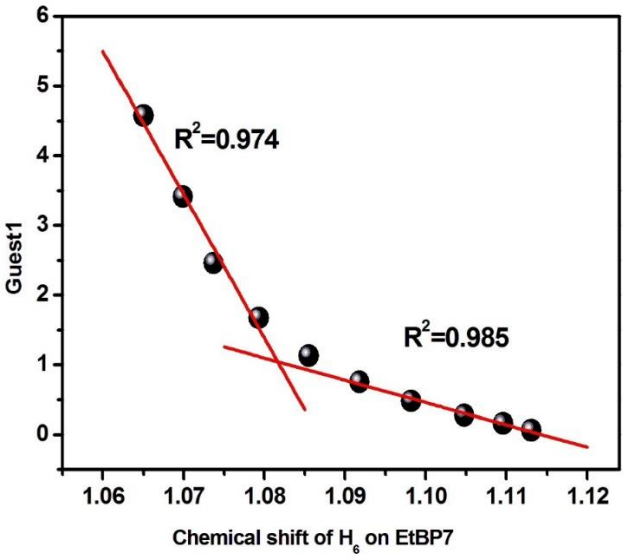

Figure S24. Mole ratio plot for **2,2'-EtBP7** and $\mathbf{1}^+$ from ^{1}H NMR (500 MHz, 298 K) experiments, wherein **2,2'-EtBP7** (at a fixed concentration) in CD_2Cl_2 was treated different molar equivalents of $\mathbf{1}^+$. The results are consistent with a 1 : 1 binding stoichiometry.

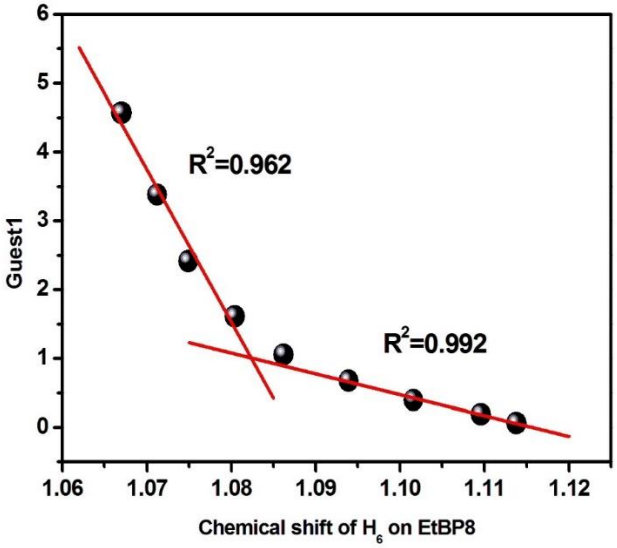

Figure S25. Mole ratio plot for **2,2'-EtBP8** and $\mathbf{1}^+$ from ^{1}H NMR (500 MHz, 298 K) experiments, wherein **2,2'-EtBP8** (at a fixed concentration) in CD_2Cl_2 was treated different molar equivalents of $\mathbf{1}^+$. The results are consistent with a 1 : 1 binding stoichiometry.

References.

[S1] C. Li, X. Shu, J. Li, J. Fan, Z. Chen, L. Weng and X. Jia *Org. Lett.*, **2012**, *14*, 4126–4129.

[S2] a) K. A. Connors, Binding Constants; Wiley: New York, **1987**. Corbin, P. S. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999; b) R. P. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi , D. J. Williams, *J. Am. Chem. Soc.*, **1996**, *118*, 4931–4951; c) Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang, H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 1807−1816.